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TITRIMETRIC ANALYSIS OF
HAN-BASED LIQUID PROPELLANTS

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Liquid propellants that are aqueous mixtures of hydroxylammonium nitrate (HAN) and triethanolammonium nitrate (TEAN) are analyzed using a combination of acid-base and Karl Fischer titrimetry, procedures that quantitatively determine the three major propellant components. The method developed converts HAN to acetoxime and nitric acid by reaction with acetone and then uses either tetrabutylammonium hydroxide or n-butylamine in ethanol or aqueous sodium hydroxide as titrant for both HAN and TEAN. Water is determined by Karl Fischer titration using the proprietary reagent "Hydranal". Each major propellant component is, therefore, determined separately. Precision, expressed as per cent, on HAN analysis obtained using the titrants tetrabutylammonium hydroxide, n-butylamine, and sodium hydroxide were 0.06, 0.1 and 0.02 respectively. Values for TEAN using the same three titrants were 0.2, 0.4 and 0.03 and precision on the water determination was 0.1%. Key words:				
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19. ABSTRACT (Con't)

When a potentiometric titration is used, acidic impurities can be detected and their relative strengths determined by their position on the titration curve. The detection limits for nitric acid, a common impurity, was determined as 0.012 moles per mole of HAN.

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I. INTRODUCTION

Liquid aqueous monopropellants containing hydroxylammonium nitrate (HAN) and the nitrate salt of an aliphatic amine are currently under consideration for use in high performance liquid propellant guns. Of the various aliphatic amine nitrates considered, triethanolammonium nitrate (TEAN) appears to be the most useful. Table 1 lists two compositions, LGP 1845 and LGP 1846, that have received the most attention. These mixtures are formulated with a HAN:TEAN molar ratio of 7, so that there is just sufficient oxygen present to convert completely all of the carbon and hydrogen to carbon dioxide and water. The third and last combustion product is nitrogen.

TABLE 1. Propellant Composition

Propellant	Composition					
	HAN (wt %)	(M)	TEAN (wt %)	(M)	Water	
1845	63.23	9.62	19.96	1.38	16.81	13.64
1846	60.79	9.09	19.19	1.30	20.02	15.93

The physical properties of these propellants have been described elsewhere.¹

Analytical procedures generally can be divided into two categories, assay methods that determine the concentration of major components, and trace methods that are intended to identify and determine concentrations of impurities and contaminants. Because assay and trace methods serve markedly different needs and cover widely different concentration ranges, the analytical procedures selected are also different. A complete assay method for propellants such as LGP 1845 or 1846 requires the quantitative determination of water, and the hydroxylammonium, triethanolammonium, and nitrate ions. Such analyses can be determined on one or more than one component in a single titration. A number of assay methods for HAN-based propellant components exist and have been used to assure quality in production. These include determination of total nitrate by ultra-violet spectroscopy^{2,3} and determination of aliphatic amine content by nuclear magnetic resonance spectroscopy.⁴ These methods require laboratory surroundings because they use complex and delicate instruments, and only provide a portion of the analytical data needed for a complete propellant assay. More recently, a complete propellant assay procedure by Fourier Transform Infrared Spectroscopy (FTIR) was developed,⁵ but it is even more complex than the methods previously mentioned. It will be of value as an on-line, interactive, quality control method within a production facility. A need exists for a simple, readily transportable assay procedure, usable by personnel who do not have access to well equipped laboratories, that will validate the quality of propellant samples.

This report is limited to the development and evaluation of propellant assay based on various titrimetric procedures. These procedures can give some indication of the presence of impurities under certain conditions but are not intended for that purpose. If the propellant has extensively reacted or if reaction products are unknown, then extreme caution must be exercised to obtain valid interpretation of titrimetric data.

II. BACKGROUND

1. THEORY OF ACID-BASE TITRIMETRY

Titrimetry is based on the existence of rapid quantitative reactions that can be readily monitored. The most common titrimetric analysis is the reaction of an acid with a base. Although the simplest monitor of such reactions is the change in color of an acid sensitive dye, greater sensitivity and reproducibility are obtained by using an electrode pair that records changes in the electromotive force (EMF) of the solution as the titration proceeds. A number of electrodes now exist that respond to specific ions, the best known and oldest of which are specific for the hydrogen ion.

Solutions of HAN or TEAN are the combinations of weak bases and nitric acid and are therefore acidic. The dissociation constant, K, is formulated as

$$K = [H^+][B^-]/[HB]$$

Using ammonia as example:

$$K = [H^+][NH_3]/[NH_4] = 5.75 \times 10^{-10}, \text{ p}K = 9.24$$

where pK is defined as $-\log K$. Values of pK and K for some relevant ions are given in Table 2.

TABLE 2. Dissociation Constants of Selected Ions in Water

Ions	pK	K
Hydroxylammonium	5.96	1.10×10^{-6}
Triethanolammonium	7.76	1.74×10^{-8}
Ammonium	9.24	5.75×10^{-10}
n-Butylammonium	10.61	2.45×10^{-11}

Recently determined⁷ pK values for aqueous HAN and TEAN are 6.11 and 7.96.

The basicity of each propellant amine relative to ammonia is readily obtained from the data in Table 2. The ability of the OH group

to withdraw electrons from the nitrogen results in hydroxylamine being 3000 times more acidic than ammonia. Replacement of an ammonia hydrogen by an alkyl group actually increases the basicity of the amine; thus, n-butylamine is four times more basic than ammonia. Again, the presence of OH groups on the amine reduces basicity; triethanolamine is 30 times less basic than is ammonia.

The propellant is a mixture of two weak acids with HAN approximately 70 times more acidic than TEAN. The hydrogen ion concentration of a mixture of two weak acids is

$$[H^+] = (K_{HAN}[HAN] + K_{TEAN}[TEAN])^{1/2}.$$

For purposes of calculation, propellant samples will be 250 mg diluted with titration solvent to approximately 50 mL so that HAN and TEAN concentrations are 3.3×10^{-2} and 4.7×10^{-3} molar, respectively. At these low concentrations, it is assumed that concentration and molarity are equal (unit activity). Thus

$$\begin{aligned}[H^+] &= (3.30 \times 10^{-2} \times 7.76 \times 10^{-7} + 4.71 \times 10^{-3} \times 1.10 \times 10^{-8})^{1/2} \\ &= 1.60 \times 10^{-4} + 7.20 \times 10^{-6} \\ &= 1.60 \times 10^{-4}.\end{aligned}$$

The hydrogen ion concentration of the mixture is equal to the hydrogen ion concentration of the HAN component alone. The concentration-pK product of HAN is 5.93 times that of TEAN in such samples, large enough that, in principle, one should be able to simultaneously determine the concentration of each of the components without interference. In practice, the accurate determination of titration end-points is influenced by a number of factors other than end-point separation. These include the rate at which hydrogen ion concentration is changing in the vicinity of the end-point and the ability of the instrumentation being used to detect small changes in hydrogen ion concentration. It is quite possible that the quantitative determination of HAN and TEAN in the presence of one another can not be achieved using simple acid-base titrimetry.

Frequently, non-aqueous solvents are used when titrimetric end-point separation cannot be obtained in water. The dielectric constant of the solvent strongly influences dissociation; dissociation constants that are close together in water often separate to an extent that end-point detection becomes feasible. Ion-pair formation is enhanced in solvents with low dielectric constants, and dissociation of ion-pairs usually affects values of pK. Vanderhoff and coworkers reported¹⁰ a decrease in conductance in aqueous solutions of HAN with increasing concentration. These authors further suggested that as concentration increases, the mobility of the ions is substantially diminished or the ions form non-conducting pairs. The use of a less polar titration solvent thus seemed to be a useful approach to the solution of the problem of overlapping end-points in HAN-TEAN titrations.

2. PREVIOUS WORK

Kasler investigated the applicability of acid-base titrations to the analysis of HAN-based liquid propellants¹¹ and developed procedures both for visual and potentiometric titrations. He could not obtain end-point separation of the two components in aqueous solvent and assessed the use of ethanol. A visual end-point titration used alcoholic KOH as titrant and phenolphthalein as indicator. The sum of HAN and TEAN concentration is determined by this procedure. In order to determine HAN in the presence of TEAN, HAN was converted to a strong acid (HNO_3) by reaction with benzaldehyde and the acid titrated using bromphenol blue as indicator. TEAN concentration is then the difference between total acid and HAN.

Potentiometric titration procedures were also developed, using a Sargent Welch Model MBP automatic titrator and tetrabutylammonium hydroxide (Bu_4NOH) in denatured alcohol as titrant. This procedure determined both HAN and TEAN. Bu_4NOH was used as titrant because KNO_3 , the reaction product of the KOH titration, is insoluble in the alcoholic solution used, producing a precipitate that blocks the fine capillary passageways of the electrode salt bridge. Although the difference in pK may have been too small to produce separate HAN and TEAN end-points in aqueous solvent, the use of denatured alcohol, a mixture consisting of 95% ethanol, water, and one or more organic additives, resulted in titration curves of which Figure 1 is typical.

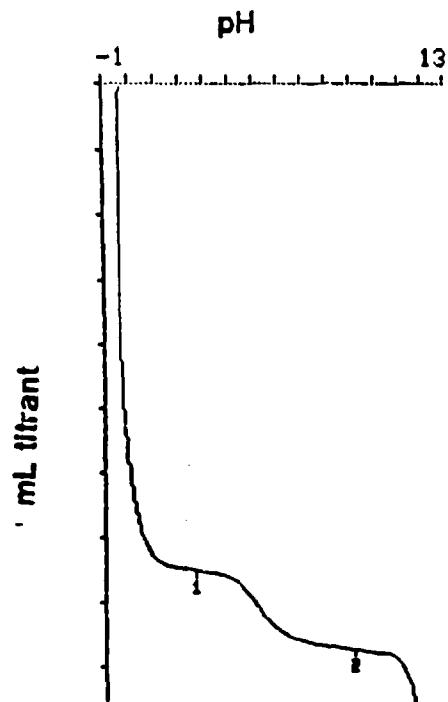


Figure 1. Titration of LGP 1845 in Denatured Alcohol with Bu_4NOH

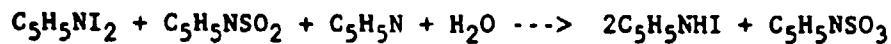
Two end-points are clearly seen so, it would seem that a successful titrimetric procedure could be developed.

Other methods for titrimetric determination of salts are based on the ability of the salts to be either oxidized or reduced. All nitrate salts can be reduced and hydroxylamine can be either oxidized or reduced depending on the experimental conditions employed. It is therefore possible to determine HAN concentration by a quantitative oxidation-reduction sequence. A titrimetric analytical procedure for HAN based on the reduction of Fe(III) to Fe(II) has been developed¹² but requires strict adherence to an empirical procedure in order to obtain reproducibility. The procedure does not determine TEAN but the TEAN does not interfere with the analysis. With proper care, accuracy and precision are excellent.¹³

Another redox method for determination of HAN involves an iodine titration of dilute solutions of HAN.¹⁴ Although precision and accuracy are not stated explicitly, review of the data indicates that the method is comparable to the iron procedure. Of the procedures mentioned, the most promising for determination of concentration of the two salts in the propellant mixture appears to be the non-aqueous acid-base titration.

3. TITRIMETRIC DETERMINATION OF WATER

The third major component of the propellant is water. The most widely used method for the determination of water is titration with Karl Fischer reagent. It has been extensively used since its discovery in 1935^{15 16} and many modifications of the original procedure exist. The Karl Fischer reagent is a combination of sulfur dioxide, iodine, and pyridine in a solvent, typically methanol; the SO₂ and I₂ both form complexes with pyridine. The reaction is believed to take place in two steps, the first involving water and the formation of a sulfur trioxide complex:



and the second involving conversion of the SO₃ complex to a stable end product:



Effective use of the reagent requires understanding of its capabilities and limitations since many compounds, in addition to water, react with one or more of the components of the Karl Fischer reagent.

One of the newer Karl Fischer titrants is "Hydranal", a proprietary reagent developed by Riedel-de Haen, Hannover, West Germany. "Hydranal" does not contain pyridine but follows a two step reaction sequence similar to the one shown. Problems occur when strongly basic amines react exothermically with the reagent, and amines are generally oxidized by iodine in methanol.¹⁶ Mixtures containing amines may be titrated

with "Hydranal" if the sample is acidified, ensuring that the amines are present only as ammonium salts. The water content in solutions of hydroxylamine salts have been successfully titrated with "Hydranal" by adding a small quantity of concentrated sulfuric acid to the titrating solvent.¹⁶

III. EXPERIMENTAL METHODS

Samples of HAN and TEAN were either obtained from Morton-Thiokol, Elkton Division, Elkton, Maryland, or were synthesized specifically for use in these studies. To prevent the introduction of spurious data, all analyses were carried out using a specially formulated LGP 1845 mixture. HAN and TEAN solutions were individually analysed prior to mixing. In addition, the total carbon content of the TEAN solution was determined using a combustion train to ascertain that no organic material other than TEAN was present. The propellant was formulated by weight to contain 61.86% HAN, 18.80% TEAN and 19.34% water.

To ascertain that acetoxime was the reaction product of HAN with acetone, an acetoxime synthesis was completed. Acetone and HAN were reacted on a molar basis in a chilled beaker. The mixture was then neutralized with 1 M NaOH and extracted with three 25 mL portions of diethyl ether. The extracts were combined and volume reduced until crystallization took place. The white, crystalline product melted at 61°C and showed no depression of the melting point of pure acetoxime.

1. ACID-BASE TITRATIONS

Kasler's original titration procedure¹¹ called for the use of alcoholic solutions of either KOH or Bu₄NOP as titrant. Both reagents are strong bases and fairly large changes in pH are observed on addition of rather small quantities of titrant to the propellant samples. It was hoped that the use of a weaker base would produce a larger separation between the HAN and TEAN end-points and a titration procedure was developed using n-butylamine as titrant. Although n-butylamine is a somewhat stronger base than ammonia, it is substantially weaker than KOH or Bu₄NOP. In addition, it has a vapor pressure low enough to permit preparation of stable solutions.

Titrations were carried out with approximately 0.2 M Bu₄NOP and 0.25 M n-butylamine. Titrant solutions were standardized weekly with both primary standard benzoic acid and potassium bichromate. Titration solvent was Fisher Commercial 95% ethanol (denatured alcohol). Solutions of HAN and TEAN were analyzed separately and in combination in propellant samples.

Additionally, the effect of sample size on the accuracy of the method was tested by analyses of 250 mg samples of propellant to which varying weights of HAN or TEAN had been added. The weight ranges of added salts were 80-800 mg and 50-400 mg for TEAN and HAN respectively.

A Metrohm* Model 672 Titrator equipped with Model 6.0102.100(LA) Glass and Model 6.0726.000 Silver/Silver Chloride electrodes was used for the non-aqueous titrations. The Ag/AgCl electrode had an internal, transition metal oxide ceramic diaphragm and an external sleeve with a ground glass joint, permitting use of a double salt bridge. The inner portion of the electrode was filled with aqueous 3M KCl and the outer sleeve with saturated ethanolic lithium chloride. The electrode and salt bridges were selected to optimize performance when using alcohol as a titration solvent. It is necessary to exclude K^+ ions from the sample since Huber had reported¹⁷ that the presence of K^+ ions gives rise to alkali error in the titrations of weak acids with glass electrodes and Harlow¹⁸ showed that the presence of as little as 10 ppm K^+ in the titration solution caused a distinct deterioration of the potentiometric break. In later work, 95% ethanol-5% water was used as solvent in place of the denatured alcohol. Prior to sample addition, 2 mL of acetone was added to 50 mL of the solvent.

Aqueous titrations were carried out using the same equipment. The special salt bridges required for non-aqueous titrations now being unnecessary, a simple Model 6.0202.100(JE) Combination Glass/Calomel electrode was used. Samples were added to approximately 50 mL water containing 2 mL acetone and titrated with 0.25 M NaOH.

2. DETERMINATION OF WATER

Titrations were carried out using the Metrohm Model 672 Titrator equipped with a sealed sample chamber and platinum conductance electrodes, the normal accessories for Karl Fischer titrations. "Hydranal", as supplied by the vendor, was used as titrant. Titration solvents were either pure methanol or methanol containing either 0.2% H_2SO_4 , 10% acetic acid, or 10% benzoic acid. About 50 to 100 mL of the solvent was placed in the reaction vessel so that the platinum electrodes were immersed. "Hydranal" reagent was added to the solvent until the residual water in the vessel had reacted and the instrument was stable. Karl Fischer titrations with "Hydranal" are normally carried out to a fixed conductance end-point and no titration curve is produced. The instrumentation as configured for conductance titrations measures conductance by monitoring voltage at minimal current flow. An arbitrary voltage value of 250 mv was set as the end-point for the titrations. Samples of HAN, TEAN, or propellant weighing 100-200 mg, were injected using a syringe through a septum into the conditioned vessel. Using this technique several samples can be analyzed consecutively without exposing the contents of the vessel to the atmosphere.

*Brinkmann Instruments, Cantiague Road, Westbury, NY, 11590

3. NITRIC ACID IMPURITIES

Nitric acid is a potential impurity in LGP 1845 and its components since the synthesis of both HAN and TEAN involve its use. It had been shown¹⁹ that the presence of nitric acid lowers the thermal stability of the propellant, so a special effort was made to determine the minimum detectable limit of nitric acid in propellant by acid-base titrimetry. Quantities of 0.1 M HNO₃ were added to 250 mg samples of either HAN solution or of the specially formulated LGP 1845 (which contained no nitric acid) and the titration carried out. Both water and 95% ethanol were used as solvents in these studies and acetone was not added to the samples.

IV. RESULTS AND DISCUSSION

1. ACID-BASE TITRIMETRY

a. Non-Aqueous Solvent: Knowledge of the pK values of HAN and TEAN in ethanol were needed to assure that a titrimetric analysis using this solvent produced accurate results. As pointed out earlier, an acid-base titration in which the pK values of two weak acids are close will result in only one end-point. Although Figure 1 makes it obvious that two end-points are obtained when ethanol is the titration solvent, it is possible that some portion of the TEAN is neutralized at the point in the titration that the HAN end-point is detected. If this is the case, then titrimetrically determined HAN concentrations will be higher and TEAN concentrations lower than their true values. The pK values of HAN and TEAN in 95% ethanol were determined at the National Bureau of Standards. The solvent used in their work was 95% ethanol-5% water rather than denatured alcohol. They found that the pK of TEAN decreases from 7.96 in aqueous solution to 6.93. This result is consistent with the decreased dissociation that is expected in a less polar solvent. The pK value obtained for HAN, however, was 6.27 compared to 6.11, an anomalous result. Clearly, HAN and TEAN end-point separation could not be obtained in 95% ethanol and the data shown in Figure 1 did not result simply from the use of a non-aqueous solvent. The solvent with which the data in Figure 1 were obtained was Fisher Commercial 95% ethanol which contains methyl isobutyl ketone as one of the denaturing agents.¹¹ Thus the results inadvertently paralleled the benzaldehyde procedure¹¹ in that an oxime and nitric acid were produced by reaction with the solvent prior to the titration.

If either 95% ethanol-5% water or a brand of denatured alcohol that did not contain methyl isobutyl ketone as a denaturant was used as solvent, a single titration end-point was obtained with HAN-TEAN mixtures. An example of the data from such a titration is shown in Figure 2.

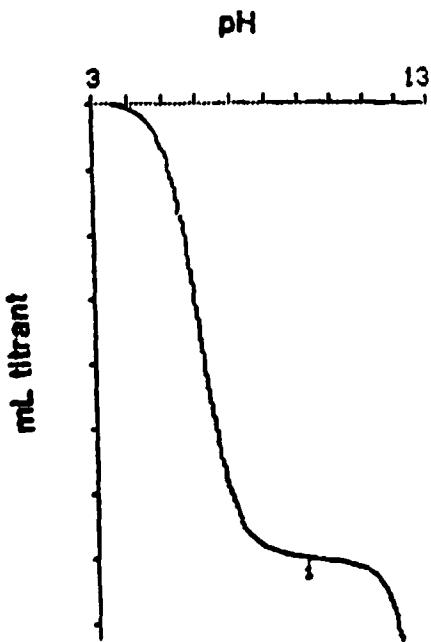


Figure 2. Titration of a HAN-TEAN Mixture Using Bu₄NOH and 95% Ethanol-5% Water as Solvent

It was considered desirable not to require specification of a composition or brand of denatured alcohol as titration solvent; a mixture of 95% ethanol-5% water was used to which was added a quantity of acetone if HAN determination was required in HAN-TEAN mixtures. HAN, in the absence of TEAN, can readily be determined without acetone addition, a fact that was used to measure the extent to which reaction with acetone was complete. Samples of HAN from a common stock produced concentrations of 80.69 and 80.64 wt%, respectively, with and without acetone addition, verifying that the reaction of HAN and acetone is quantitative under the titration conditions used. The acetoxime that is the product of the HAN-acetone reaction is so weakly acidic that its neutralization end-point does not appear on the titration curves obtained. The end-point observed when HAN is added to the acetone-ethanol mixture is due to the neutralization of nitric acid released by acetoxime formation, whereas the end-point detected when HAN samples are titrated in the absence of acetone is the result of neutralization of the weakly acidic HAN. The pH at which the end-points are observed is 6.95 with acetone and 9.08 without. TEAN samples titrated in solvent with and without acetone produced identical titration curves, indicating that acetone addition will not interfere with the determination of TEAN in the propellant analysis.

An assay analysis is required to measure concentration accurately over a reasonable range. To determine linearity of response and the ability of the titrimetric procedure to measure HAN and TEAN accurately in the presence of one another, a series of titrations was carried out on LGP 1845 to which varying quantities of either HAN or TEAN had been added. The resulting data are shown in Figures 3 and 4.

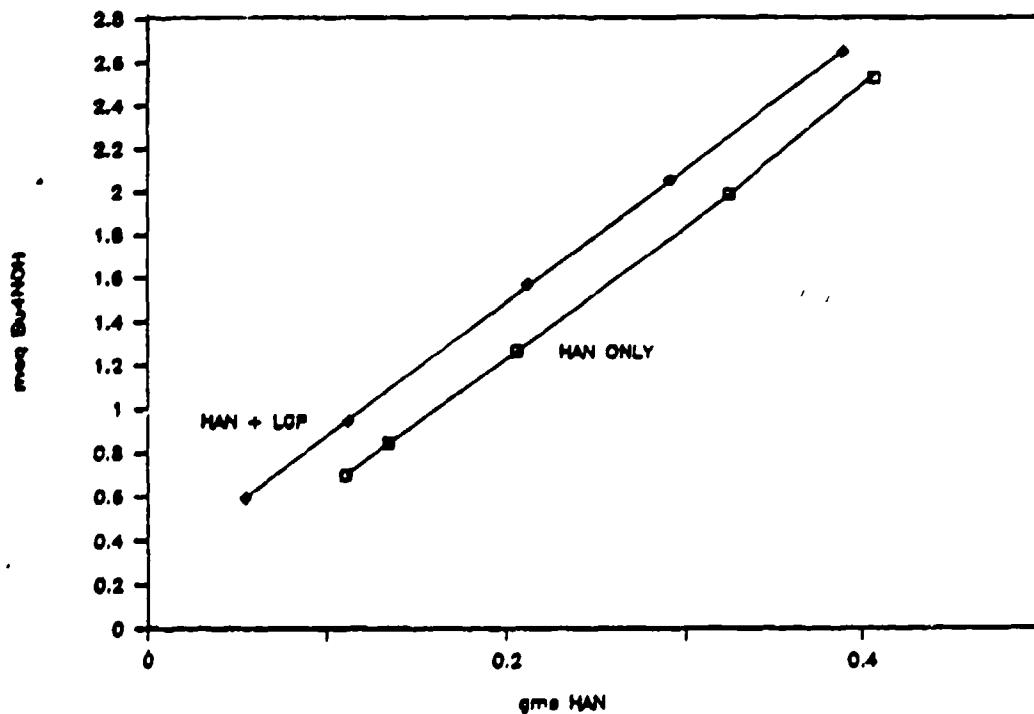


Figure 3. Bu₄NOH Titrations Using a Range of HAN Concentrations

One sees from the Figures that response varies linearly with concentration of either of the propellant components and that the presence in the sample of the other component does not affect response.

Titrations were carried out using Bu₄NOH, a strong base, and n-butylamine, a much weaker base, as titrants. The titration curves obtained are shown in Figure 5.

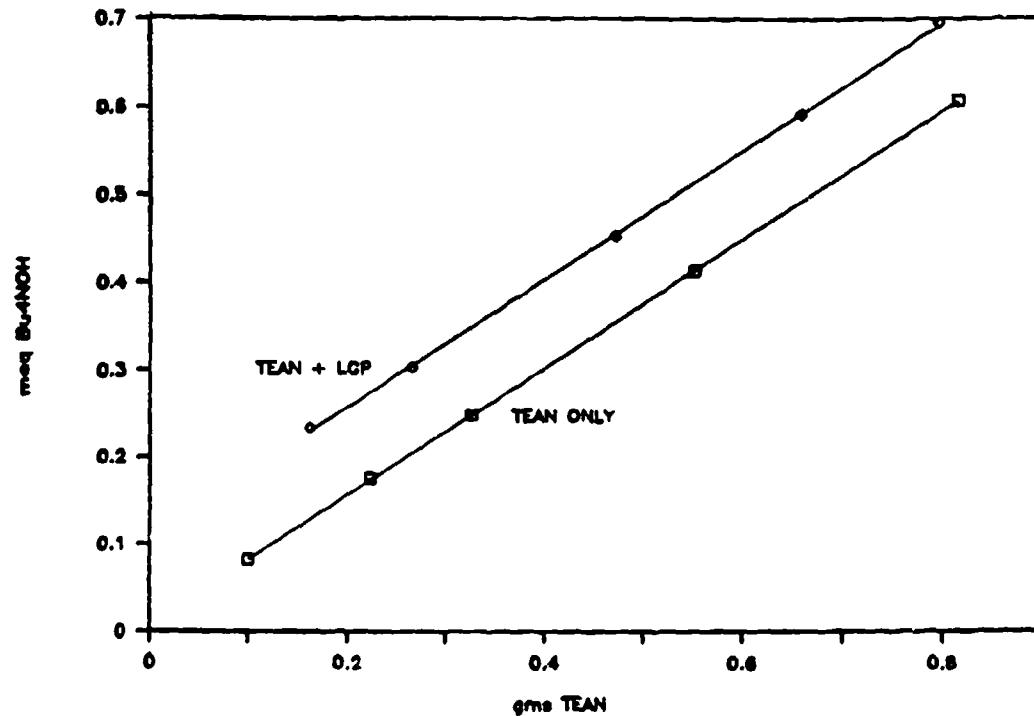


Figure 4. Bu_4NOH Titrations Using a Range of TEAN Concentrations

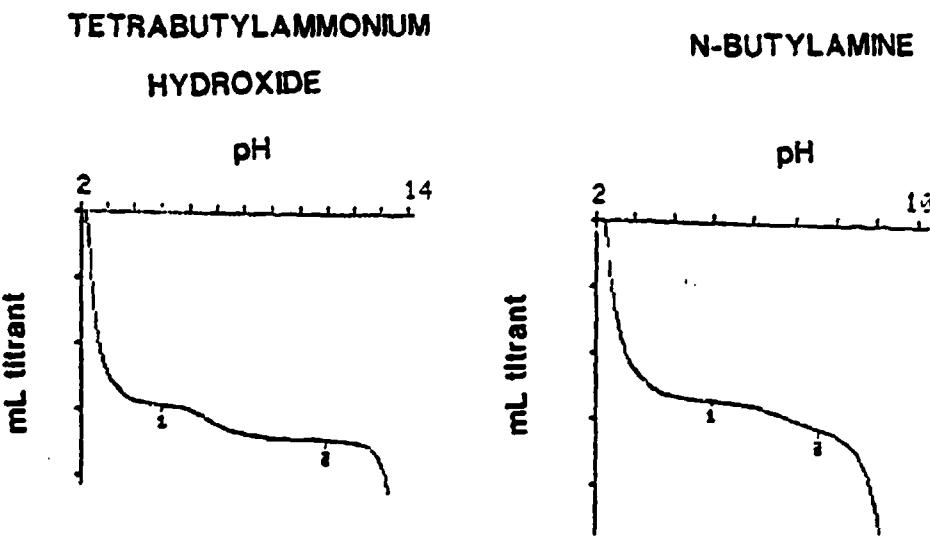


Figure 5. Titrations Curves For LGP 1845 Using Bu_4NOH and n-Butylamine as Titrants

As expected, the end-points obtained with the stronger base are more sharply defined. The HAN and TEAN concentrations determined with Bu_4NOH are 60.52 and 20.12% and with n-butylamine are 61.82 and 18.34%. The results with either titrant are within the same experimental error so that neither titrant is favored when using the titration equipment described herein. It should be pointed out, however, that the burets that are part of the Metrohm Model 672 Titrator have a delivery accuracy of 0.001 mL and are thus able to add very small increments of the strong base to the sample being analysed. The use of equipment of lesser quality could show a measurable difference in response using the two titrants.

b. Aqueous Solvent An example of an aqueous titration in which acetone is added to the titration solvent is shown in Figure 6.

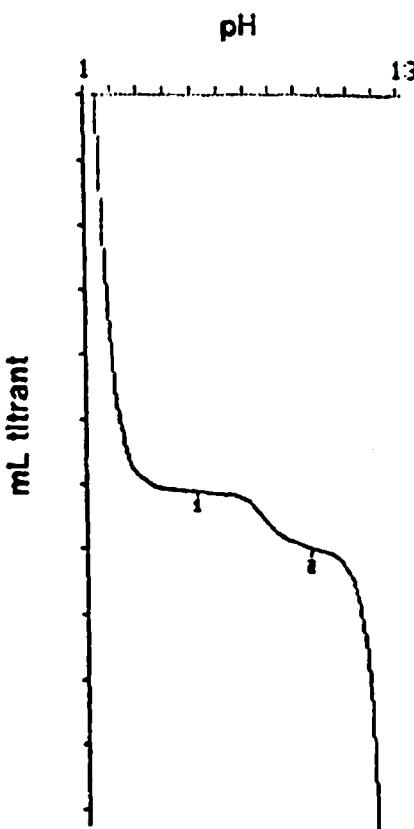


Figure 6. Titration Curves For LGP 1845 Using Aqueous NaOH and Water-Acetone Solvent

The separation between the nitric acid and TEAN end-points are clearly seen and are sufficiently spaced that no error in HAN determination from partial neutralization of TEAN is expected. HAN and TEAN concentrations determined by this procedure are 60.76 and 18.95%.

2. WATER ANALYSIS

The Karl Fischer titrations using "Hydranal" showed no significant differences with any of the several acids added to the methanol solvent although differences were noted when acid was absent. The presence of acid in the solvent improves both precision and accuracy and produces a clearly superior titrimetric procedure. The 10% glacial acetic acid-90% methanol mixture was chosen arbitrarily as solvent. The method is both precise and accurate and appears to be quite insensitive to impurities or minor variations in procedure.

3. NITRIC ACID DETECTION

The detection limit for nitric acid in a 250 mg sample of 80 weight percent HAN is 0.012 mole HNO_3 per mole of HAN; the 250 mg value was chosen since it approximates the sample size usually used in propellant analysis. Since HAN concentration in the 50 mL of solvent is 0.0417 M and the pK of HAN in 95% ethanol is 6.27, the hydrogen ion concentration due to the HAN is 1.5×10^{-4} M. The pH change produced by addition of nitric acid to the sample at the detection limit is comparable to the pH of the HAN sample and indicates that the equipment is operating properly. The detection limit is higher in water (0.014 mole/mole HAN) than in 95% ethanol and is higher if sample size is increased. Both of these observations are expected and are in accord with theoretical considerations. The nitric acid detection limit can be lowered by addition of a known quantity of acid to the titration solvent. Under such conditions, nitric acid is determined by difference, a procedure generally not considered desirable because it is subject to rather large error if not carried out precisely.

4. PRECISION AND ACCURACY

Addressing first the matter of precision one notes that precision improves when the variables are all of the same order of magnitude. Reduction of the number of variables will also improve precision. Since the propellant and its components were homogeneous liquids that were not permitted to change concentration by solvent evaporation throughout the course of the studies conducted, it is reasonable to assume that sample concentrations were constant. All samples used for acid-base titrimetry were weighed directly into their reaction vessels so that sample size uncertainty is limited to weighing error which is conservatively estimated at 0.1 mg or 0.04% of the nominal 250 mg samples used. Uncertainty in sample size for the Karl Fischer determinations was probably somewhat higher because these samples were injected into the titration vessel, a less precise procedure. Uncertainty in the volume of titrant added was 0.001 mL in a nominal 5 mL of titrant used (0.02%). The remaining sources of imprecision are end-point detection and end-

point overlap. The matter of end-point overlap in titrations with multiple end-points has been discussed earlier and its reduction to insignificance is the reason that the titrimetric procedure evolved to its current status. End-point detection combines the sensitivity of the instrumentation used, the algorithms within the instrumentation for end-point determination, and the amount of change of pH with addition of base in the vicinity of the end-point. The first two of these three factors are inherent in the instrumentation and were kept constant throughout the study. The third factor relates directly to the steepness of the neutralization curve and error is reduced when the potentiometric break is well defined. The determination of TEAN is most severely affected by end-point detection because the slope of its neutralization curve is lower than that for HAN. The reasons for the gentler TEAN slope are that both its concentration is lower and its molecular weight is higher than those of HAN.

The precision obtained for determination of HAN and TEAN in replicate samples using various titrants is given in Table 3.

TABLE 3. Analytical Precision Obtained

Titrant	HAN (%)	TEAN (%)	Water (%)
Bu ₄ NOH	0.06	0.2	
n-Butylamine	0.1	0.4	
NaOH(aqueous)	0.02	0.03	
Hydralan			0.1

As seen in the Table, TEAN results are less precise than for HAN regardless of the titrant used; the aqueous NaOH titrant produces the most precise results. The results correlate without exception to the end-point detection criteria discussed.

The consideration of analytical accuracy is quite a different matter. Accuracy requires comparison of data with an accepted standard value and, in the case of the analyses under consideration here, no accepted standard value is available. Efforts were made in formulating the propellant mixture to assure purity of the reagents and to establish HAN and TEAN concentrations as carefully as possible. The extent to which this effort was successful is not known. Analytical results obtained using the various titrimetric procedures are presented in Table 4.

TABLE 4. Titrimetric Analysis of LGP 1845

Titrant	HAN (%)	TEAN (%)	Water (%)
Bu ₄ NOH	60.52	20.12	
n-Butylamine	61.82	18.34	
NaOH(aqueous)	60.76	18.95	
Hydralan			19.26
As Formulated	61.86	18.80	19.34

One observes that the n-butylamine data result in higher HAN and lower TEAN concentrations than are obtained with the other titrants. We believe that some small end-point overlap is observed when this weaker base is used, which results in a skew of the data in favor of HAN. Also the TEAN values are higher when Bu_4NOH is the titrant. These results are consistent with data obtained using samples of TEAN in which only one end-point is obtained. We cannot find a reasonable explanation for such apparent high values. Comparison of the results obtained with the "as formulated" values seems to indicate that the n-butylamine results are the most accurate. There are, however, no compelling reasons to consider the "as formulated" values more accurate than the experimental values presented in Table 4 so their agreement with the n-butylamine data may be fortuitous.

Titrimetry has long been an accepted analytical method. If the chemical reactions being observed are clearly understood and titrants are properly standardized using appropriate primary standards, then titrimetric analysis is considered among the most accurate methods available. We conclude that HAN-TEAN propellant analysis using aqueous sodium hydroxide as titrant and water containing sufficient acetone to produce quantitative conversion of HAN to nitric acid as solvent is the most accurate assay procedure presently available. It is reasonable to calibrate various specialized instrumental methods using assay data thus obtained.

V. CONCLUSIONS

An assay method for determination of HAN, TEAN, and water in aqueous liquid propellants has been developed. The dissociation constants of the two salts are too close to one another to permit their simultaneous determination by simple acid-base titrimetry. If acetone or some other simple ketone is present in excess in the titration solvent, the HAN is quantitatively converted to an oxime and nitric acid. The dissociation constants of nitric acid and TEAN are sufficiently separated to permit simultaneous, quantitative analysis. Water or 95% ethanol are suitable as titration solvent although water is preferred. The third component of the propellant, water, is determined by Karl Fischer titration using the proprietary reagent "Hydranal" and methanol-10% glacial acetic acid solvent. Precision for the HAN titrations was determined as 0.06, 0.1 and 0.02% for tetrabutylammonium hydroxide, n-butylamine and sodium hydroxide respectively. Values for TEAN with the same titrants were 0.2, 0.4 and 0.03%. Precision on the water analysis was 0.1% using "Hydranal" reagent.

Free nitric acid present as a trace impurity is accurately determined with a detection limit of 0.012 mole per mole of HAN if 95% ethanol without added acetone is used as titration solvent. The titrimetric procedures are simple, rapid, lend themselves to automation, can be carried out by personnel with little training and utilize equipment that is both relatively portable and rugged. The procedures

described are valid only as assay methods for reasonably pure propellant or propellant components. They are not suitable, nor were they designed, for use with propellant that has undergone substantial chemical reaction or is contaminated to a significant extent.

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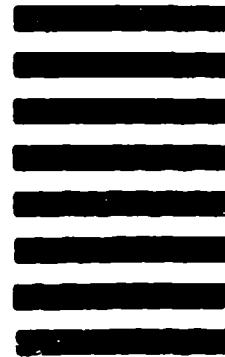


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